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(54) ELECTROLYTIC SOLUTION AND ELECTROCHEMICAL ELEMENT USING IT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolytic solution with P less tendency to generate hydrogen fluoride by hydrolysis.

SOLUTION: Boron compound(s) shown in a formula 1 ($X+[(Rf)_nBF_4-n]^-$) is dissolved in a non-aqueous solvent. In the formula, X^+ shows alkali metal ion or onium ion, Rf shows perfluoroalkyl group, and n shows integer of 1 to 4. When n is not less than 2, plural Rfs may be mutually different and plural Rfs may be mutually bonded to form a ring structure together with boron.

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CLAIMS

[Claim(s)]

[Claim 1] The electrolytic solution characterized by the boron compound shown by the formula (1) in a non-aqueous solvent dissolving.

$X+[(Rf)_nBF_4]^-$ -- (1)

X⁺ shows alkali-metal ion or onium ion among [type, Rf shows a perfluoroalkyl radical, and n shows the integer of 1 thru/or 4. In addition, when n is two or more, you may differ mutually, and two or more Rf may join mutually together, and two or more Rf may form the ring structure with boron.]

[Claim 2] The electrolytic solution characterized by the boron compound shown by the formula (2) in a non-aqueous solvent dissolving.

$X+[(CF_3)_mBF_4]^-$ -- (2)

[-- X⁺ shows alkali-metal ion or onium ion among a formula, and m shows 1 or 2.]

[Claim 3] The electrolytic solution according to claim 1 or 2 characterized by being the ion chosen from the group to which X⁺ changes from a lithium ion, the fourth class ammonium ion, and the fourth class friend JINIUMU ion.

[Claim 4] The electrolytic solution according to claim 1 to 3 characterized by the ester chosen from the group to which a non-aqueous solvent changes from a carbonate and carboxylate being what occupies 50 % of the weight or more.

[Claim 5] The electrochemistry component characterized by using the electrolytic solution according to claim 1 to 4.

[Claim 6] The electrochemistry component according to claim 5 to which an electrochemistry component is characterized by being a lithium secondary battery, an electric double layer capacitor, or an electrolytic capacitor.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to electrochemistry components, such as the electrolytic solution which the boron compound containing a fluorine is dissolving in the non-aqueous solvent and a lithium cell using this electrolytic solution, an electric double layer capacitor, and an aluminium electrolytic capacitor.

[0002]

[Description of the Prior Art] As nonaqueous electrolyte used for an electrochemistry

component, many things are known from the former. For example, as nonaqueous electrolyte of a lithium cell, what dissolved the hexa fluorophosphoric acid lithium in the mixed solvent of ethylene carbonate and diethyl carbonate (the volume Masayuki Yoshio and for Akiya Ozawa, a rechargeable lithium-ion battery, Chapter 6, 83 pages, 1996, Nikkan Kogyo Shimbun), the thing (WO 98/No. 15562 official report) which dissolved the perfluoroalkyl fluorophosphoric acid lithium in ethylene glycol wood ether etc. are known. As the electrolytic solution of an electric double layer capacitor, what dissolved the quaternary ammonium salt of tetrafluoroboric acid in propylene carbonate etc. (the Ue sincerity, electrochemistry, 66 **, 904 pages, 1998) is known. Moreover, as the electrolytic solution of an aluminium electrolytic capacitor, what dissolved the quaternary ammonium salt (the Ue sincerity, a new capacitor, 3 **, No. 2, 55 pages, 1996) of organic acids, such as a phthalic acid, and the fourth class friend JINIUMU salt in gamma-butyrolactone, ethylene glycol, etc. (WO 95/No. 15572 official report, JP,9-283379,A) is known.

[0003]

[Problem(s) to be Solved by the Invention] Although the nonaqueous electrolyte used for an electrochemistry component is manufactured so that the moisture content may decrease as much as possible, it usually still contains the moisture of dozens of ppm. Moreover, since the moisture which the moisture in an ambient atmosphere might mix into nonaqueous electrolyte, and has adhered to the components of an electrochemistry component etc. may be eluted in nonaqueous electrolyte in case an electrochemistry component is manufactured using nonaqueous electrolyte, the moisture of dozens of ppm or more exists, so that you may surely say the nonaqueous electrolyte used for the electrochemistry component.

[0004] When moisture exists in the nonaqueous electrolyte used for the electrochemistry component, there is a problem that the electrolyte which is dissolving is hydrolyzed. For example, it hydrolyzes like a bottom type and the hexa fluorophosphoric acid lithium used for the nonaqueous electrolyte of a lithium secondary battery generates hydrogen fluoride.

$\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{LiF} + \text{POF}_3 + 2\text{HF}$ hydrogen fluoride is rich in reactivity, the metal part of an electrochemistry component is made to corrode, or the reaction of making nonaqueous electrolyte decompose etc. which is not desirable is caused. If these reactions occur, many properties of an electrochemistry component, for example, electric capacity, charge-and-discharge effectiveness, withstand voltage, etc. will fall, or a poor appearance, such as expansion of the component by the generation of gas, will happen. Therefore, even if the moisture of a minute amount exists, the nonaqueous electrolyte which cannot cause hydrolysis easily is called for. This invention tends to meet such a demand.

[0005]

[Means for Solving the Problem] The electrolytic solution concerning this invention is characterized by the boron compound shown by the formula (1) in a non-aqueous solvent dissolving.

$\text{X}^+[(\text{Rf})_n\text{BF}_4]^-$ -- (1)

X⁺ shows alkali-metal ion or onium ion among [type, Rf shows a perfluoroalkyl radical, and n shows the integer of 1 thru/or 4. In addition, when n is two or more, you may differ mutually, and two or more Rf may join mutually together, and two or more Rf may form the ring structure with boron.]

[0006]

[Embodiment of the Invention] In the electrolytic solution concerning this invention, the boron compound containing the fluorine shown by the above-mentioned formula (1) as an electrolyte is used. As a cation shown by X^+ , for example A lithium, sodium, a potassium, Alkali-metal cations, such as caesium; Tetramethylammonium, Ethyl trimethylammonium, diethyl dimethylammonium, triethyl methylammonium, Tetraethylammonium, tetrapropylammonium, tetrabutylammonium, N and N-dimethylpyrrolidinium, N-ethyl-N-methyl pyrrolidinium, Fourth class ammonium cation, 1-ethyl-2-methyl imidazolium, such as N and N-dimethyl piperidinium and N-ethyl-N-methyl piperidinium, The fourth class friend JINIUMU cations, such as 1-ethyl - 2, 3-dimethyl imidazolinium, 1, 2 and 3, and 4-tetramethyl imidazolinium; Tetramethylphosphonium, The fourth class phosphonium cations, such as ethyl trimethyl phosphonium, diethyl dimethyl phosphonium, triethyl methyl phosphonium, tetraethyl phosphonium, tetra-propyl phosphonium, and tetrabutyl phosphonium, etc. are mentioned. As for X^+ , in the case of the electrolytic solution of a lithium cell, it is desirable that it is a lithium ion especially. Moreover, it is desirable that they are [in the case of the electrolytic solution of an electric double layer capacitor] the fourth class friend JINIUMU ion, such as 1-ethyl - 2 and 3-dimethyl imidazolinium, in the case of the electrolytic solution of the fourth class ammonium ion, such as triethyl methylammonium, and an aluminium electrolytic capacitor.

[0007] As a perfluoroalkyl radical shown by R_f , perfluoroalkyl radicals of carbon numbers 1-12, such as a trifluoromethyl radical, a pentafluoroethyl radical, a heptafluoro propyl group, a nonafluorobutyl group, an undeca fluoro pentyl radical, a perfluoro hexyl group, a perfluoro octyl radical, a perfluoro decyl group, and a perfluoro undecyl radical, are mentioned. Moreover, as what two or more R_f combined mutually, an octafluoro tetramethylen radical, a decafluoro pentamethylene radical, etc. are mentioned. (1) As for the sum total of the carbon of the fluorination hydrocarbon group shown by R_f , in the compound of a formula, it is desirable that it is 12 or less. As an example of (1)-type compound which has these fluorination hydrocarbon groups Trifluoromethyl trifluoro borate, bis(trifluoromethyl) difluoro borate, Tris (trifluoromethyl) fluoroborate, tetrakis (trifluoromethyl) borate, Pentafluoroethyl trifluoro borate, bis(pentafluoroethyl) difluoro borate, Tris (pentafluoroethyl) fluoroborate, tetrakis (pentafluoroethyl) borate, Heptafluoro propyl trifluoro borate, bis(heptafluoro propyl) difluoro borate, Tris (heptafluoro propyl) fluoroborate, tetrakis (heptafluoro propyl) borate, Nona fluoro BUCHIRUTORI fluoroborate, bis(nona fluoro butyl) difluoro borate, Tris (nona fluoro butyl) fluoroborate, undeca fluoro PENCHIRUTORI fluoroborate, Bis(undeca fluoro pentyl) difluoro borate, perfluoro hexyl trifluoro borate, Bis(perfluoro hexyl) difluoro borate, perfluoro octyl trifluoro borate, Perfluoro DESHIRU trifluoro borate, perfluoro undecyl trifluoro borate, Trifluoromethyl pentafluoroethyl difluoro borate, bis(trifluoromethyl) pentafluoroethyl fluoroborate, Tris (trifluoromethyl) pentafluoroethyl borate, trifluoromethyl bis(pentafluoroethyl) fluoroborate, Bis(trifluoromethyl) bis(pentafluoroethyl) borate, Trifluoromethyl tris (pentafluoroethyl) fluoroborate, Tetrakis (pentafluoroethyl) borate, perfluoro (B and B-tetramethylen) difluoro borate, Perfluoro [bis(B and B-tetramethylen) borate], perfluoro (B and B-pentamethylene) difluoro borate, perfluoro [bis(B and B-pentamethylene) borate], etc. are mentioned. Generally, (1)-type compound is in the inclination for the electrical conductivity of the

electrolytic solution which makes this an electrolyte to fall as molecular weight becomes large. Therefore, as an electrolyte, it is desirable to use trifluoromethyl trifluoro borate or bis(trifluoromethyl) difluoro borate. In addition, (1)-type compound can also use two or more sorts together.

[0008] (1) The compound shown by the formula is compoundable by the well-known approach. For example, trifluoromethyl trifluoro borate is R.D.Chambers. et It is compoundable to al., J.Am.Chem.Soc., and 82 and 5298 (1960) by the approach of a publication. Bis(trifluoromethyl) difluoro borate is G.Pawellke. et It is compoundable to al., J.Organomet.Chem., and 178 and 1 (1979) by the approach of a publication. Moreover, the cation (X⁺) of the compound shown by (1) formula is convertible for other cations by the well-known proper approach. For example, after considering as the solution from which the solution of (1)-type compound was processed by the cation exchange resin of H mold, and the cation was changed into the hydrogen ion and adding the hydroxide of a desired cation, or the solution of a hydrogencarbonate to this, (1)-type compound which has a desired cation can be obtained by distilling off a solvent. Moreover, as an exception method, the salt of a desired cation is added in the solution of (1)-type compound, and after settling the cation of (1)-type compound as an insoluble salt and removing it, (1)-type compound which has a desired cation can also be obtained by distilling off a solvent. (1) Since to be a high grade very much is demanded when using the compound of a formula as an electrolyte of an electrochemistry component, refine and use even for desired purity (1)-type compound usually obtained by the above by recrystallization, solvent extraction, etc.

[0009] As a solvent of the electrolytic solution, for example Dimethyl carbonate, ethyl carbonate methyl, diethyl carbonate, Diphenyl carbonate, carbonic acid methylphenyl, ethylene carbonate, propylene carbonate, Carbonates, such as 2, 3-dimethyl ethylene carbonate, a carbonic acid butylene, carbonic acid vinylene, and 2-vinyl ethylene carbonate; Methyl formate, Methyl acetate, methyl propionate, ethyl acetate, propyl acetate, butyl acetate, Amyl acetate, methyl benzoate, ethyl benzoate, gamma-butyrolactone, Carboxylate, such as gamma-valerolactone and delta-valerolactone; Ethylene glycol wood ether, Ethylene glycol diethylether, ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, 1,4-dioxane, 1, 3-dioxolane, A tetrahydrofuran, 2-methyl tetrahydrofuran, 2, 6-dimethyl tetrahydrofuran, Ether, such as tetrahydropyran, ethylene glycol, propylene glycol, Alcohols, such as a glycerol; An acetonitrile, propionitrile, Nitril; N-methyl formamides, such as methoxy propionitrile, guru taro nitril, an adiponitrile, and 2-methyl guru taro nitril, N-ethyl formamide, N.N-dimethylformamide, N,N-dimethylacetamide, Amides, such as N-methyl pyrrolidinone; A dimethyl sulfone, an ethyl methyl sulfone, Sulfones, such as diethyl sulfone, sulfolane, 3-methyl sulfolane, 2, and 4-dimethyl sulfolane; Dimethyl sulfoxide, Sulfoxides, such as a methylethyl sulfoxide and diethyl sulfoxide; A dimethyl sulfate, Sulfates, such as diethyl sulfate, sulfuric-acid ethylene, and a sulfuric-acid propylene; Sulfurous-acid dimethyl, Sulfites, such as sulfurous-acid diethyl, sulfurous-acid ethylene, and a sulfurous-acid propylene; Trimethyl phosphate, Phosphoric ester, such as phosphoric-acid ethyl dimethyl, diester phosphate methyl, and phosphoric-acid triethyl; 1,3-dimethyl-2-imidazolidinone, 1, 3-dimethyl - 3, 4, 5, 6-tetrahydro-2(1H)-pyrimidinone, 3-methyl-2-oxazolidinone, nitromethane, etc. are mentioned. These solvents can also use two or more sorts together. It is desirable to make a carbonate, carboxylate, or these into a subject also

in these solvents, namely, to use that whose 50 % of the weight or more is a carbonate and carboxylate.

[0010] The electrolytic solution concerning this invention dissolves the boron compound containing the above-mentioned fluorine in the above-mentioned solvent. Generally, the concentration of the boron compound in the electrolytic solution is the range where it does not deposit by a temperature change etc. since the one where the electrical conductivity of the electrolytic solution is higher is desirable, and its higher possible one is desirable. When using trifluoromethyl trifluoro borate and bis(trifluoromethyl) difluoro borate as a boron compound, the concentration of these compounds in the electrolytic solution is usually 0.1-3mol/L, and is 0.5-2mol/L preferably.

[0011] The electrochemistry component concerning this invention carries out opposite arrangement of a positive electrode and the negative electrode through a separator fundamentally, and has the structure where the electrolytic solution prepared above by this was infiltrated. the case of lithium ion batteries, such as a lithium primary cell, a rechargeable lithium-ion battery, and a lithium polymer rechargeable battery, -- as positive active material -- transition-metals oxide [, such as multiple oxide; MnO₂ of lithiums, such as LiCoO₂, LiNiO₂, LiMnO₂, and LiMn₂O₄, and transition metals, and V₂O₅,]; -- disulfide compounds [, such as conductive polymer; Pori (2,5-dimercapto-1,3,4-thiadiazole),], such as transition-metals sulfide; polyacetylenes, such as MoS₂ and TiS, the poly acene, the poly aniline, polypyrrole, and the poly thiophene, etc. are used. As a negative-electrode active material, corks, such as carbide of high molecular compounds, such as occlusion and the carbonaceous ingredient which can be emitted, for example, a graphite, phenol resin, and furan resin, pitch coke, petroleum coke, and needle coke, a carbon fiber, glassy carbon, pyrolytic carbon, activated carbon, etc. are used in a lithium metal, lithium alloys, such as a lithium aluminium alloy, or a lithium. It is desirable to use what dissolved (1)-type compound whose a cation (X⁺) is a lithium as the electrolytic solution in the mixed solvent of annular carbonates, such as ethylene carbonate and propylene carbonate, and chain-like carbonates, such as dimethyl carbonate, ethyl carbonate methyl, and diethyl carbonate.

[0012] It is desirable to use a carbonaceous material in that are inactive electrochemically and it has moderate conductivity to the electrolytic solution as an ingredient of the polarizable electrode used for a positive electrode and a negative electrode in the case of an electric double layer capacitor. Activated carbon with a large area of the electrode interface which a charge accumulates is desirable especially. It is desirable to use what dissolved (1)-type compound whose a cation (X⁺) is the fourth class ammonium, the fourth class friend JINIUMU, or the fourth class phosphonium in propylene carbonate as the electrolytic solution.

[0013] In the case of an aluminium electrolytic capacitor, aluminium foil is used as the aluminium foil which formed the insulating alumina layer in the front face by anodizing etc. as a positive electrode, and a negative electrode. For expansion of surface area, such aluminium foil usually carries out etching processing, and is used. It is desirable to use what dissolved (1)-type compound whose a cation (X⁺) is the fourth class ammonium, the fourth class friend JINIUMU, or the fourth class phosphonium as the electrolytic solution in gamma-butyrolactone, ethylene glycol, sulfolanes, or ones of these mixed solvents.

[0014] As a separator used for an electrochemistry component, the product made of paper,

the product made from polypropylene, the product made from polyethylene, the product made from a glass fiber, etc. should just use a thing in ordinary use. Moreover, as an electric conduction assistant used in case an electrode is manufactured with an electrode active material, it is desirable to use metal fibers, such as carbon black, such as acetylene black and KETCHIEN black, a natural graphite, a thermal-expansion graphite, a carbon fiber, ruthenium oxide, titanium oxide, aluminum, and nickel, etc. It is desirable especially to use the acetylene black or KETCHIEN black which can secure desired conductivity by little combination. Although an electric conduction assistant is blended so that it may usually become 5 - 50 % of the weight to an electrode active material, it is desirable to blend so that it may become 10 - 30 % of the weight.

[0015] Moreover, as a binder used with an electric conduction assistant, it is desirable to use polytetrafluoroethylene, polyvinylidene fluoride, a carboxymethyl cellulose, fluoro olefine copolymer crosslinked polymer, polyvinyl alcohol, polyacrylic acid, polyimide, a petroleum pitch, a coal pitch, phenol resin, etc. It is desirable to use the polymer (**) of polytetrafluoroethylene, polyvinylidene fluoride, and other fluorine content monomers or the copolymer of these monomers and other monomers especially. Since the dissolved electrolytes are water and difficulty reactivity, the electrolytic solution concerning this invention has the small inclination to generate hydrogen fluoride, even if the water of a minute amount exists in the electrolytic solution. Therefore, the electrochemistry component manufactured using this electrolytic solution continues at a long period of time, is stabilized and can maintain that property.

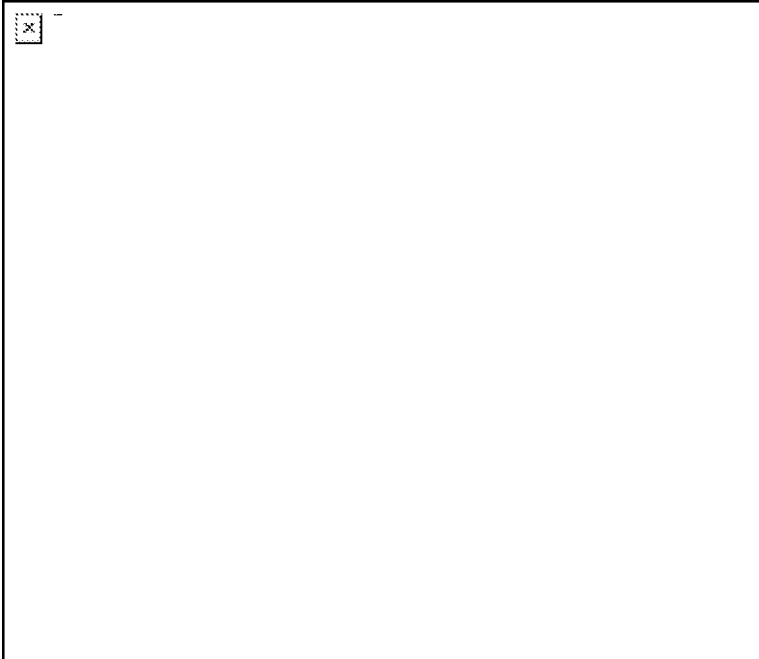
[0016]

[Example] Although an example explains this invention still more concretely below, this invention is not limited to these examples.

[0017] Electrolytic solution; the electrolytic solution was prepared using the solvent and electrolyte which are shown in Table 1, and the electric conductivity and the moisture content in 25 degrees C were measured. Moreover, the content of hydrogen fluoride was measured by the ion chromatography method, the content of hydrogen fluoride was again measured about what held this electrolytic solution at 70 degrees C in the well-closed container made from stainless steel further for 50 hours, and the augend of the hydrogen fluoride concentration by heating was computed. A result is shown in Table 1.

[0018]

[Table 1]



[0019] Lithium secondary battery; the lithium manganese multiple oxide (LiMn_2O_4) 90 weight section, the acetylene black 5 weight section, and the polyvinylidene fluoride 5 weight section were mixed, N-methyl pyrrolidinone was added to this, and it considered as the slurry. After applying and drying this at aluminium foil, it pierced in a circle with a diameter of 12.5mm, and considered as the positive electrode. After holding the positive electrode and the negative electrode (the diameter of 12.5mm, lithium metal plate with a thickness of 1.0mm) in the case made from stainless steel (1.6mm in the diameter of 20mm, thickness) through the separator (porous polypropylene sheet with a thickness of 0.3mm) and making this carry out vacuum impregnation of the electrolytic solution of NO.1 of Table 1 to it, the lid was put through the gasket made from polypropylene, and the ***** coin mold lithium secondary battery was manufactured. When the charge and discharge test was performed about this cell in charge and discharge current consistency 0.6 mA/cm² and the electrical-potential-difference range 4.3-3.5V, initial discharge capacity was 123 mAh/g and the charge-and-discharge effectiveness of 20 cycle eye was 97%. On the other hand, although initial discharge capacity was almost the same at 122 mAh/g when the trial same about the lithium secondary battery completely similarly manufactured except having used the thing of NO.4 of Table 1 as the electrolytic solution was performed, the charge-and-discharge effectiveness of 20 cycle eye was as low as 88%, and was large. [of cycle degradation]

[0020] Electric double layer capacitor; the coconut-shell-activated-charcoal powder (specific-surface-area 1700m²/g, 10 micrometers of mean diameters) 80 weight section, the acetylene black 10 weight section, and the polytetrafluoroethylene 10 weight section were mixed, it kneaded and cast, and the positive electrode and the negative electrode were manufactured. After holding the positive electrode and the negative electrode in the case made from stainless steel (1.6mm in the diameter of 20mm, thickness) through the separator (nonwoven fabric made from polypropylene with a thickness of 0.3mm) and making this carry out vacuum impregnation of the electrolytic solution of NO.2 of Table

1 to it, the lid was put through the gasket made from polypropylene, and the electric double layer capacitor of a ***** coin mold was manufactured. The constant-voltage continuation impression trial was performed over 50 hours by 70 degrees C and applied-voltage 3.0V about this, and change of electrostatic capacity was investigated. The electrostatic capacity computed from the 5mA constant-current discharge curve was 1.3F before the trial, and the electrostatic-capacity maintenance factor after a trial was 98%. On the other hand, although the electrostatic capacity before a trial was the same as 1.3F when the trial same about the electric double layer capacitor completely similarly manufactured except having used the thing of NO.5 of Table 1 as the electrolytic solution was performed, the electrostatic-capacity maintenance factor after a trial was as low as 92%, and its degradation was comparatively large.

[0021] The capacitor made from aluminum; vacuum impregnation of the electrolytic solution of NO.3 of Table 1 was carried out to the aluminum electrolysis capacitor element (what stopped the etched aluminium foil which has the alumina layer which is a dielectric on a front face, the separator made of paper, and the etched aluminium foil on winding and a tape) of case size 10mmphix16mmL, rated voltage 10V, and rated electrostatic-capacity 1000F specification. This was held in the case made from aluminum through the obturation rubber made of isobutylene isoprene rubber, and the aluminium electrolytic capacitor of CEO4 mold was manufactured by caulking *****.

When the load test of 1000 hours was performed at 105 degrees C about this thing and the impedance in 100kHz was measured, trial before was 0.05 ohms and the trial back was 0.07ohms. on the other hand, the thing (the electric conductivity in 25 degrees C -- 9.1 mS/cm) which is used from the former as the electrolytic solution and which dissolved 1-ethyl -2 and 3-dimethyl imidazolinium phthalic-acid hydrogen salt in gamma-butyrolactone so that it might be set to 0.5 mols / L Although the impedance before a trial was 0.05ohms when the aluminium electrolytic capacitor completely similarly manufactured except having used the moisture content of 50 ppm performed the same trial, the impedance after a trial was increasing to 0.10 ohms.

[Translation done.]
